

TITANIUM ALUMINIDE MATERIAL RESISTANT  
TO MOLTEN ALUMINUM

FIELD OF THE INVENTION

The present invention relates to materials, tooling and methods for use in contact with molten aluminum and its alloys in manufacture of products therefrom.

BACKGROUND OF THE INVENTION

In the making of metal matrix composites (MMC's) comprising fine ceramic (e.g. alumina) reinforcement particles dispersed in a matrix comprising aluminum or its alloys, a semi-solid slurry (a thixotropic liquid/solid mixture) of the molten aluminum matrix material is formed in a refractory crucible, and the ceramic reinforcement particles are introduced into the partially molten aluminum slurry and mechanically mixed therein by a rotating mixing blade immersed in the slurry. Introduction of the ceramic reinforcement particles into the slurry enables a high volume percentage, such as 30-40 volume %, of reinforcement particles to be dispersed in the aluminum matrix of the final MMC. Such an MMC process is described in the Flemings U.S. Patent 3 948 650.

The mixing blade immersed in the partially molten slurry is subjected to abrasive action from the ceramic particles as they are dispersed in the partially molten slurry. Expensive flame sprayed alumina coated stainless steel (Type 304) mixing blades used in the past typically exhibit catastrophic wear after only 30 minutes such that replacement with a new mixing blade is required.

There is a need for improved materials and tooling for use in contact with molten aluminum and its alloys as well as partially molten slurries thereof.

An object of the present invention is to satisfy this need.

SUMMARY OF THE INVENTION

The present invention provides in one embodiment a titanium aluminide alloy for contact with molten aluminum and its alloys wherein the titanium aluminide alloy includes a rare earth element in an effective amount to prolong resistance of the alloy to attack by the molten aluminum and its alloys.

An illustrative embodiment of the invention provides tooling for use in contact with molten aluminum and its alloys where the tooling comprises a titanium aluminide alloy including yttrium in an amount of about 1.5 to about 5.5 weight % of the alloy to prolong resistance to attack of the tooling to molten aluminum and its alloys.

In another illustrative embodiment of the invention, the titanium aluminide alloy or tooling is heated in an oxygen-bearing atmosphere (e.g. air) at elevated temperature to form a passivating surface oxide film in-situ thereon prior to contact with molten aluminum and its alloys. The titanium aluminide alloy or tooling is periodically removed from service in contact with the molten aluminum or aluminum alloy, cleaned and reheated in an oxygen-bearing atmosphere at elevated temperature to prolong its service life.

Tooling pursuant to the present invention can comprise a mixing blade for making MMC's in the manner described above and also can comprise other tooling, such as die casting machine components including a die, core element, shot sleeve, and plunger for the die casting of aluminum and its alloys. In a method of die casting pursuant to the invention, one or more of the die, core element, shot sleeve and plunger is/are made from the rare earth-bearing titanium aluminide alloy described above.

The above and other objects and advantages of the present invention will become more readily apparent from the following drawings taken in conjunction with the following detailed description.

#### DESCRIPTION OF THE DRAWINGS

The Figure is a schematic view of apparatus for making an MMC by mixing ceramic reinforcement dispersoids in a semi-solid slurry comprising aluminum using a titanium aluminide alloy mixing blade pursuant to the invention.

#### DESCRIPTION OF THE INVENTION

The present invention provides a titanium aluminide alloy and tooling made therefrom for contact with molten aluminum and its

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alloys, such as for immersion in molten aluminum and its alloys. Molten aluminum and its alloys include commercially pure aluminum metal and alloys of aluminum with other metals and/or elements where aluminum is present as a majority of the alloy. Representative aluminum alloys include, but are not limited to, alloys 319, 320 and others. The titanium aluminide material and tooling made therefrom comprise a titanium aluminide alloy that includes a rare earth element in an effective amount to prolong resistance of the material and tooling to attack by the molten aluminum and its alloys. The titanium aluminide alloy comprises an intermetallic compound comprising Ti and Al. For example, the titanium aluminide alloy typically comprises a predominantly gamma phase TiAl alloy, although other titanium aluminide alloys may be used in practicing the invention. Titanium aluminide alloys comprising about 30% to about 35% by weight Al, 55% to 65% by weight Ti, one or more alloying elements such as W, Nb, Cr, Si, B, V and others, and a rare earth element in effective amount can be used to practice the invention depending on particular temperatures and stresses to be encountered in service.

Preferably, the titanium aluminide alloy comprises a predominantly gamma phase TiAl intermetallic compound containing a small amount (e.g. up to 15 volume %) of alpha  $Ti_3Al$  phase. The rare earth element can be selected from the group consisting of yttrium (Y) and rare earth elements of atomic number 57 to 71 of the Periodic Table. For example, the titanium aluminide alloy can include Y, one or more of the rare earth elements including mischmetal, and combinations of Y and one or more rare earth elements.

In an illustrative embodiment of the invention offered for purposes of illustration and not limitation, the material comprises predominantly gamma phase TiAl alloy including yttrium in an amount of about 1.5 to about 5.5 weight % of the alloy.

For example, a gamma TiAl alloy with different amounts of Y therein was evaluated for resistance to molten aluminum in immersion testing. In particular, a particular predominantly gamma

09740708-121900

phase TiAl alloy (base alloy) was modified to include 1.5%, 3.5%, 5.5% and 7.5% by weight Y. The Y-modified alloy was made by melting charges of a gamma TiAl base alloy comprising, in weight %, 33.6% Al, 0.5% Cr, and 0.1% Nb and adding Y to respective charges to achieve the above 1.5%, 3.5%, 5.0% and 7.5 weight % Y concentrations. Each Y-modified alloy was melted and cast/solidified in ceramic shell molds to form cylindrical bars having a diameter of 1/4 inch and a length of 4 inches and also blocks having dimensions of 2 inches by 1 inch by 3 inches. The cast cylindrical bars were used as specimens. In addition, the cast blocks were cut into specimen slabs having dimensions of 1 inch by 2 inches by 1/2 inch.

The specimens included a surface oxide film or layer formed by heating the specimens in a furnace in air to 1830 degrees F (1000 degrees C), holding at that temperature in air for 18 hours, and cooling in the furnace to below 500 degrees F.

Specimens of each Y-modified alloy were immersed in molten aluminum alloy 380 at 700 degrees C (1300 degrees) and removed periodically for examination for reaction with the melted aluminum alloy. The molten aluminum alloy was still (i.e. not stirred) during immersion of the specimens therein. The Table below sets forth the number of days that the various specimens and unmodified base alloy (0 weight % Y) did not exhibit visible attack or reaction with the molten aluminum, :

TABLE

Y Weight %	Time Without Visible Attack
0	3 days
1.5	7 days
3.5	7 days
5.0	14 days
7.5	7 days

From the Table, it is apparent that the specimens of the base alloy devoid of Y (0 weight % Y) exhibited visible attack by the

molten aluminum within 3 days. In contrast, the specimens of the base alloy including 1.5%, 3.5% and 5.0% Y by weight pursuant to the invention exhibited resistance to the molten aluminum for prolonged times. The inclusion of Y in the base alloy appeared to increase the resistance of the surface oxide film on the specimens to attack by the molten aluminum, although Applicants do not wish to be bound by any theory in this regard. The inclusion of Y in the base alloy in an amount of 7.5% by weight Y was not further beneficial in that the surface oxide film or layer was observed to spall off of the 7.5 weight % Y base alloy specimens in the molten aluminum.

Furthermore, specimens of the base alloy including 3.5% by weight Y were heated in air at 1000 degrees C for 18 hours prior to immersion in the molten aluminum to form in-situ a passivating surface oxide film or layer. These specimens were left immersed in the molten aluminum alloy 380 for 7 days and then removed and cleaned by mechanical scraping to remove adherent aluminum alloy and expose a fresh surface of the titanium aluminide alloy specimen. The cleaned specimens then were again heated in air at 1000 degrees C for 18 hours prior to reimmersion in the molten aluminum alloy. Repetition of these heat treatment/cleaning steps was discovered to be effective to prolong the life of the specimens for many weeks (e.g. 3 weeks) before visible attack of the specimens was observed. Only very minor dimensional changes of the specimens were observed after these heat treatment/cleaning steps.

Figure 1 illustrates schematically apparatus for making a metal matrix composite (MMC) by mixing ceramic reinforcement dispersoids in a semi-solid slurry comprising aluminum using a passivated rare earth-bearing titanium aluminide alloy mixing blade pursuant to an embodiment of the invention. For example, the apparatus is shown comprising a mixing container 10, such as a refractory crucible, from which the semi-solid slurry mixed with ceramic reinforcement dispersoids is countergravity cast into a mold (not shown) as described, for example, in U.S. 5 042 561, the teachings of which are incorporated herein by reference. The mixing container 10 is

09740708-121900

disposed on a rotary ceramic table 12 in a vacuum chamber 14 connected by conduit or port VP to a conventional vacuum pump P. The rotary table is rotated by a motor 16 and belt 19 through a vacuum sealed bearing 18. An induction coil 20 is positioned in the chamber 14 about the container 10 to inductively heat a solid charge comprising aluminum or aluminum alloy (hereafter referred to as aluminum charge). The induction coil 20 receives electrical power via electrical cables (not shown) that pass through electrical power port EP. The solid aluminum charge is positioned in the container 10 comprising silicon carbide ceramic material substantially non-reactive with the molten aluminum charge and is melted in air by energization of the induction coil 20. After the aluminum charge is melted, a lid or cover 14a of the vacuum chamber 14 is lowered and vacuum tight sealed on the chamber 14. A relative vacuum (subambient pressure) then is drawn in chamber 14 by actuation of the vacuum pump P. A typical vacuum level of 0.050 to 0.080 torr is provided in chamber 14.

Energization of the induction coil 20 then is controlled in a manner to cool the melted aluminum charge M to form a semi-solid aluminum slurry comprising a partly solid/partly liquid charge (i.e. thixotropic slurry). For aluminum alloy 356 (nominally comprising 7 weight % Si, 0.3 weight % Mg and balance aluminum), the aluminum charge is melted (melting temperature of 1135 degrees F) and is cooled while stirring with mixer blade 30 to 1110 degrees F by controlled de-energization/energization of the induction coil 20 to form the semi-solid slurry in the container 10. As the melted aluminum charge is cooled, it is mixed by rotation of the table 12 and mixer blade 30 to provide a thixotropic slurry comprising about 30% to 40% by volume solid phase and balance liquid or molten phase, although these percentages of solid/liquid phases in the slurry are offered only for purposes of illustration and not limitation. The mixer blade 30 is fastened to and rotated by shaft 32 extending through the lid 14a and a drive train 33 coupled to a suitable motor 34 outside of the chamber 14. The temperature of the semi-solid aluminum slurry is determined by thermocouple T.

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Preheated ceramic reinforcement powder 50 is introduced from a hopper 40 outside of chamber 14 through a supply tube 42 extending into the chamber 14 to overlie the container 10. The hopper 40 is evacuated to the same vacuum level as is provided in the chamber 14 before the preheated reinforcement powder 50 is introduced into the crucible 10. A conventional pinch valve 52 between the hopper 40 and the supply tube 42 is opened to supply the preheated powder to the crucible. The preheated reinforcement powder is introduced under the same vacuum as in chamber 10 to ensure that the powder is dry and flows smoothly onto the top of the aluminum slurry in the container 10.

An illustrative reinforcement powder for use in making MMC's comprises alumina powder having particle size in the range of 5 to 20 microns diameter, although any particular reinforcement powder or any particular particle size range may be used. Other reinforcement powder which can be used in making MMC's include, but are not limited to, silicon carbide and other ceramic particles. The reinforcement powder is rapidly mixed into the semi-solid aluminum slurry in the container 10 by combined rotation of the table 12 and the mixing blade 30. After thorough mixing, the aluminum/particle slurry is heated by induction coil 20 to the liquid temperature range for casting the alloy. The liquid melt having the reinforcement powder mixed therein then is cast from the container 10 by removing lid 14a and immersing a suction tube (not shown) in the liquid aluminum/dispersed powder charge in the crucible and countergravity casting the charge into an evacuated ceramic shell or other casting mold positioned thereabove as described in U.S. Patent 5 042 561, whose teachings are incorporated herein by reference to this end.

In accordance with an embodiment of the invention, the mixer blade 30 can comprise a titanium aluminide alloy including a rare earth element in an effective amount to prolong resistance of the mixer blade to attack and degradation by the slurry. For example, the mixer blade 30 can be made of investment cast predominantly gamma phase titanium aluminide alloy including a rare earth

09740708-121900

addition as described above. The mixer blade 30 can be passivated by forming a surface oxide film thereon. The surface oxide film is formed in a thickness range of about 1 micron to 100 microns and passivates the titanium aluminide alloy mixer blade 30. The passivating surface film can be formed on the mixer blade 30 by cooling an as-investment cast blade while hot to ambient temperature in air and using the mixer blade in the as-cast and oxidized (passivated) condition. Alternately, the surface film can be formed by machining the cast mixer blade to desired configuration followed by heating the machined mixer blade to an elevated temperature such as from about 800 degrees F, for example at 1000 degrees F and above, in air or other oxygen bearing atmosphere for a time (e.g. 18 hours in air at 1830 degrees F) effective to form the passivating surface film.

Tooling pursuant to the present invention can comprise the mixer blade for making MMC's in the manner described above. Tooling also can comprise other components, such as conventional die casting machine components for die casting aluminum and its alloys including a die, a core element disposed in the die, a shot sleeve communicated to a die cavity defined in the die and a plunger movable in the shot sleeve to move molten material in the shot sleeve into the die cavity. In the die casting of aluminum and its alloys pursuant to a method of the invention, the molten aluminum or aluminum alloy is introduced into the shot sleeve and the plunger in the shot sleeve is moved to introduce the molten aluminum or alloy into the die cavity where an optional core element is present and where the molten aluminum or alloy at least partially solidifies to form a die cast article. Pursuant to the invention, one or more of the die, core element, shot sleeve, and plunger are made of the above-described titanium aluminide alloy including a rare earth element, such as Y, in an effective amount to prolong resistance to attack as described above.

The passivated titanium aluminide intermetallic tooling of the invention is advantageous in that such tooling is used without any need to coat the tooling with a bulk protective coating of any



kind. That is, the oxide surface film formed in-situ on the tooling comprises the passivating surface film on the tooling of the invention and is advantageous to yield more dimensional precise parts or components.

Although the invention has been described in detail above with respect to certain embodiments, those skilled in the art will appreciate that modifications, changes and the like can be made therein without departing from the spirit and scope of the invention as set forth in the appended claims.

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